



ORIGINAL ARTICLE

Effect of operating parameters on the selectivity of nanofiltration phosphates transfer through a Nanomax-50 membrane



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Abstract The present study deals with the retention by nanofiltration of synthetic solutions containing phosphate salts with a Nanomax-50 charged membrane. This work investigates the potential of the membrane for the selective retention of the phosphate anions H_2PO_4^- and HPO_4^{2-} . The first part of the study involves the characterization of the membrane used in filtration tests with aqueous solutions of neutral solutes (organic) and charged solutes (inorganic salts). In the second part, the effects of pressure, ionic strength and pH on the retention of phosphate anions are described. The results showed that the membrane is negatively charged at $\text{pH} > 5$ with a pore radius of about 0.45 nm and a hydraulic permeability around $24.6 \cdot 10^{-12} \text{ m s}^{-1} \text{ Pa}^{-1}$. The values of the rejection rate of the phosphate anions are about 93% for HPO_4^- and 98% for HPO_4^{2-} . The rejection rate of phosphate anions, particularly monovalent, depends on chemical parameters (feed concentrations, ionic strength and pH) and on transmembrane pressure. The experimental

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results were analyzed by the Spiegler–Kedem model and the transport parameters of phosphate anions: the reflection coefficient σ and solute permeability P_s were determined.

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1. Introduction

The constant increase in the amounts of wastewaters produced by industries and urban communities presents serious risks on health and environment. Owing to the increasingly severe regulations, recycling wastewaters for irrigation (agricultural areas, open spaces, plantations, etc.) and the treatment of industrial wastewaters for reuse (or simply to reduce chemical pollution) became a priority for any urban community and any industrial sector. Among possible solutions, the membrane filtration processes are getting more and more important in virtue of their increasingly competitive energy and techno-economic performance (Schafer et al., 2005; Nabi et al., 2010, 2011; AL-Othman et al., 2011).

The increasing diversity of membrane technology requires targeting and adapting the membranes and separation processes for each specific application. The present work is aimed to study a membrane separation applied to the recovery and to recover specific effluents charged with phosphates present in municipal and industrial wastewaters (Guastalli et al., 2009). The presence of phosphate in wastewaters contributes to the depletion of oxygen in water resulting in harm to living organisms.

Nanofiltration is a membrane separation process at the molecular scale. Its advantage lies in its ability to achieve selective separation of small size electrically charged species and/or neutral molecular species. It is used for removing organic pollutants (pesticides, herbicides, and halogenated organic compounds) (Ahmad et al., 2008; Causseranda et al., 2005) and inorganic (nitrate, zinc, copper and cadmium) (Paugam, 2002; Ben Farèse, 2006; Mehiguene et al., 1999; Garba, 1999) dissolved in water discharge. Organic nanofiltration membranes are characterized by a pore size in the nanometer range and generally have charged groups on surface. The high selectivity of nanofiltration membranes is thus based on both size exclusion and exclusion mechanisms based on electrostatic charged species of opposite sign to the membrane (Donnan mechanism) (Schafer et al., 2005; Wang et al., 1995).

The present study deals with the retention of phosphate anions: HPO_4^- and $\text{H}_2\text{PO}_4^{2-}$ by nanofiltration. These anions have the characteristic of being variable-charged species depending on the pH and the forms of which they are interrelated through the acidity constants of phosphoric acid: $\text{p}K_{a1} = 2.1$, $\text{p}K_{a2} = 7.2$, $\text{p}K_{a3} = 12.4$.

The first part of this study involves the characterization of the Nanomax-50 membrane used with aqueous solutions of neutral solute (sugars) and charged solute (inorganic salts). No previous researches have been reported on the use of the above membrane in the present specific situation. The results showed that the membrane is negatively charged, with a pore radius of about 0.45 nm, a hydraulic permeability around $24.6 \cdot 10^{-12} \text{ m s}^{-1} \text{ Pa}^{-1}$ and a retention rate, at pH ranging between 5 and 6 for the considered salts, increasing in the following order:

$$R(\text{Na}_2\text{SO}_4) = 98\% > R(\text{NaCl}) = 65\% > R(\text{CaCl}_2) = 30\%.$$

In the second part, the effects of the charge, the pressure, the ionic strength and the pH, on the retention of phosphate anions, were studied. The values of the rejection rates of phosphate anions were about 93% for HPO_4^- at pH = 5.5 and 98% for $\text{H}_2\text{PO}_4^{2-}$ at pH = 8.5. The retention rates of the phosphate anions and in particular, the monovalent depend on the chemical parameters (feed concentrations, pH) and on the trans-membrane pressure. The pH, the concentration and the nature of the ions in solution have a dominating effect on the selectivity of the tested Nanomax-50 membrane. At pH values above 5, due to the ionization of the groups R-COO^- of the membrane (pI 4.9), the co-ions anions of the membrane control the retention R. This is due to their electrophoretic mobility (charge/size) and to the valence of the counter-ion (cation of the solution): $R(\text{Cl}^-) = 65\%$ for NaCl and 30% for CaCl_2 . At pH values ranging between 4 and 5, the net charge of the membrane is close to zero, the ions transmission, thus, is controlled primarily by steric exclusion. At pH values less than 4, the phosphates are retained in the form H_3PO_4 , $R(\text{H}_3\text{PO}_4) = 40\%$. This induces a positive retention of the ions H^+ , $R(\text{H}^+) = 46\%$ and a negative retention of the monovalent phosphate anions $R(\text{HPO}_4^-) = -4.76\%$ to offset the charge imbalance created between the solution and the membrane. The Increase in the ionic strength in the phosphates solutions: $I(\text{NaH}_2\text{PO}_4)$ ml M/L [0.20 → 11] and $I(\text{Na}_2\text{HPO}_4)$ [0.60 → 32] ml M/L induced a decrease in retention of relatively low phosphate anions $R(\text{HPO}_4^-)$ [94% → 88%] et $R(\text{H}_2\text{PO}_4^{2-})$ [99% → 91%]. This is due to the screening of groups present on the membrane, which leads to the fact that the selectivity mechanisms of the nanofiltration on the Nanomax-50 membrane seem to be mainly controlled by Donnan effect.

2. Material and methods

2.1. Operating protocol

The used nanofiltration membrane is a composite spiral organic Nanomax-50 membrane (Millipore) of filtration area 0.37 m^2 and a cut-off MWCO = 300 Da. It has a macroporous polyester mechanical support, a microporous polysulfone.

The filtration experiments were performed on a commercial pilot apparatus Millipore Proscale with 12 L capacity (Fig. 1), on solutions of neutral solutes (saccharose, glucose) (Prolabo) and inorganic salts (NaH_2PO_4 , Na_2HPO_4 , Na_2SO_4 , NaCl and CaCl_2) (Fluca Analytical, Merck and Acros organics) in discontinuous mode, with a total return of the retentate and permeate into the feed tray at a flow rate of 380 L h^{-1} , a pressure ranging from 2 to 10 bars and a temperature of $25 \pm 0.5 \text{ }^\circ\text{C}$.

The saccharose and glucose were selected because they were located in a range of molecular weights framing the cut threshold of the Nanomax-50 membrane (MWCO = 300 Da).

The pH effect was studied in the range of 3–12 using a solution of H_3PO_4 of 100 mg L^{-1} . The basicity was adjusted by

adding NaOH. Analytical monitoring of anions was performed by ion chromatography with conductimetric detection (DIONEX), whereas the determination of total organic carbon was provided by a TOC analyzer, model: 1010, OI ANALYTICAL BIORITECH.

2.2. Results analysis

The considered parameters are:

- the permeation flux, deduced from experimental measurements of volume (ΔV) performed on a fixed range time (Δt) given by the equation:

$$J_v = \frac{\Delta V}{(\Delta t \times S)}$$

where S represents the membrane surface;

- the observed retention rate, calculated from the following relation:

$$TR = 1 - \frac{C_p}{C_0}$$

where C_p and C_0 indicate the permeate concentration and initial concentration, respectively.

3. Results and discussion

3.1. Characterization of the Nanomax-50 membrane

3.1.1. Permeability of the Nanomax-50 membrane

The pure solvent flux J_w increases linearly with increasing pressure (Fig. 2) and follows the Darcy law: $J_w = L_p \times \Delta P$.

The hydraulic permeability of the membrane L_p was calculated from the slope of the straight line in Fig. 2 and equals $24.6 \cdot 10^{-12} \text{ m s}^{-1} \text{ Pa}^{-1}$ which is closer to what was found by many authors (Paugam, 2002; Ben Farèse, 2006; Mehiguene et al., 1999; Garba, 1999).

3.1.2. Evaluation of the pore size of Nanomax-50 membrane

Uncharged solutes of different size namely: saccharose and glucose were filtered through the Nanomax-50 membrane. The combined use of the Spiegler–Kedem model (Schaepe et al., 1998; Chaabane et al., 2006) and of the SHP model (Steric Hindrance Pore) (Wang et al., 1995) allowed to determine the pore radius to be 0.45 nm. Fig. 3 displays a good correlation between the model and the experimental values of the retention rate of the solute as function of solvent flux. Thus, the reflexion coefficient σ could be determined for each solute (Table 1).

4. Effect of the charge

The shape of the curves in Figs. 4 and 5 reflects the forces influencing the transport of species through the Nonomax-50 membrane. The retention rate of the salts: NaH_2PO_4 , NaCl and CaCl_2 , increases with the increasing flux and then levels off (convection forces), however, that of Na_2HPO_4 and Na_2SO_4 remains relatively constant with increasing flux (diffusion forces). Reading the retention values of the various studied salts (Fig. 4) confirms the negative charge of Nonomax-50 membrane for $\text{pH} > 5$ (Paugam, 2002; Ben Farèse, 2006).

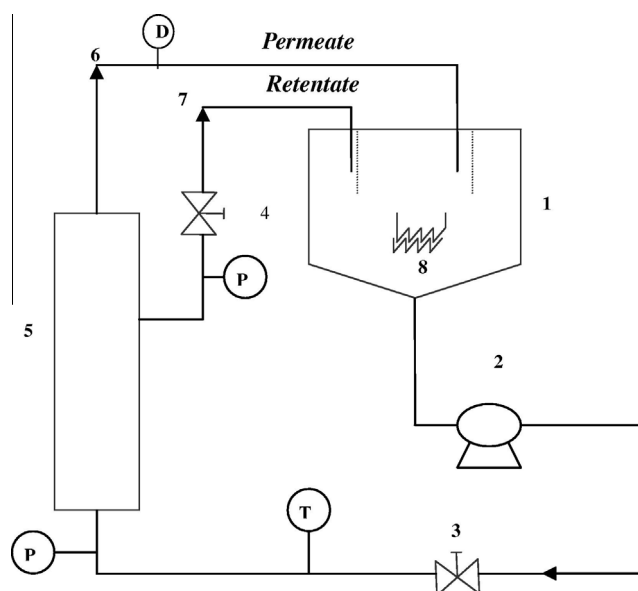


Figure 1 Synoptic diagram of the nanofiltration pilot. (1) Feed tray, (2) positive-displacement pump, (3 and 4) pressure regulating valves, (5) nanofiltration module, (6) recirculation of permeate, (7) recirculation of retentate, (8) heat exchanger, (D) flowmeter, (P) pressure sensor, and (T) temperature sensor.

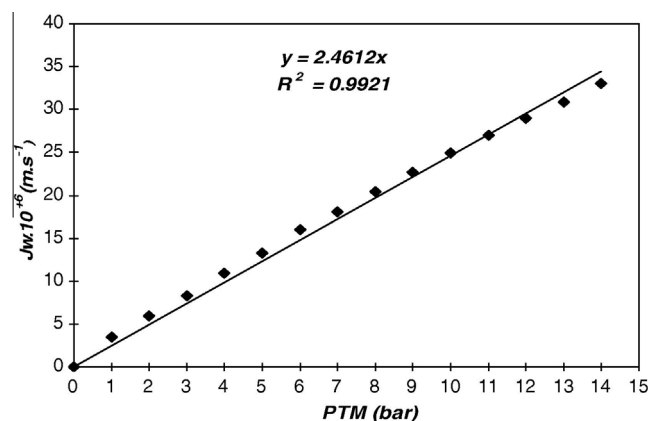


Figure 2 Variation of water flux as a function of the transmembrane pressure for the Nanomax-50 membrane.

$$\text{TR}(\text{Na}_2\text{SO}_4) = 98\% > \text{TR}(\text{NaCl}) = 65\% > \text{TR}(\text{CaCl}_2) = 30\%$$

The comparison of retention rates of phosphate anions HPO_4^{2-} ($R = 98\%$) and HPO_4^- ($R = 93\%$) (Fig. 5) shows that the pH affects the membrane charge. In fact, the divalent anions ($\text{pH} = 8.5$) are strongly retained compared with monovalent ($\text{pH} = 5.5$). This phenomenon is explained by a shift of acid–base equilibrium between the carboxylic function forming the polymer of the membrane active surface and basic phosphate salts of the medium. This induces an electric field and subsequently produces a large charge density of negative sign of the membrane. On the other hand, the HPO_4^{2-} hydration radius ($r_h(\text{HPO}_4^{2-}) = 0.327 \text{ nm}$, is larger than that of HPO_4^-

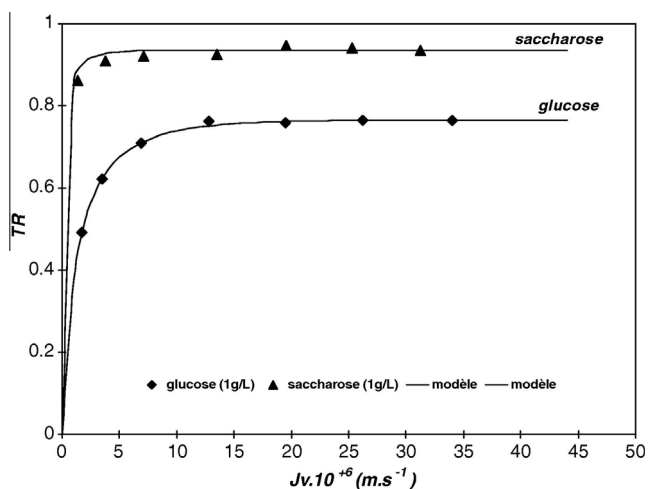


Figure 3 Evolution of the retention rate of glucose and saccharose as a function of volumetric flux.

Table 1 Reflexion coefficient σ for both neutral solutes by the Spiegler–Kedem model.

Solute	Reflexion coefficient (σ)
Saccharose	0.935
Glucose	0.765

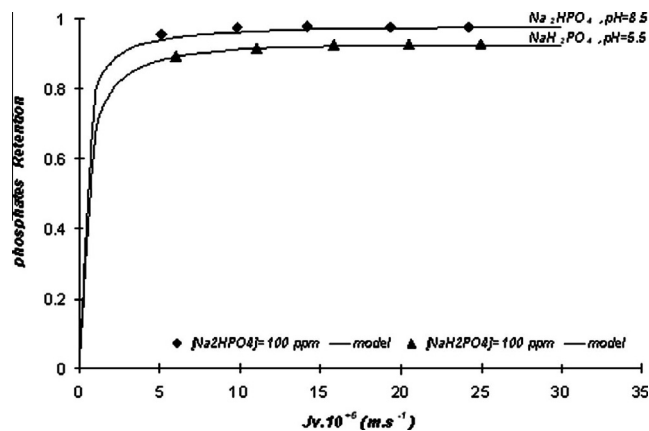


Figure 5 Retention rate of the salts: NaH_2PO_4 and Na_2HPO_4 by the Nanomax-50 membrane.

Table 2 Transport parameters σ and P_s for the two phosphate salts by the Spiegler–Kedem model.

Solute	Reflexion coefficient (σ)	$P_s 10^{+8}$ (m/s)
NaH_2PO_4	0.9271	5.35
Na_2HPO_4	0.9763	0.882

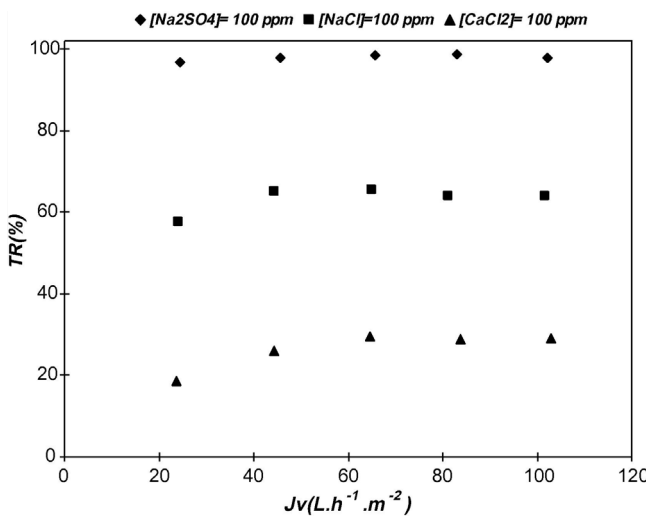


Figure 4 Effect of the charge on the retention rate of salts: Na_2SO_4 , NaCl and CaCl_2 by the Nanomax-50 membrane at pH (5.5–6.5).

$r_h(\text{H}_2\text{PO}_4^-) = 0.302 \text{ nm}$ Kiriukhin and Collins (2002). This parameter puts more emphasis on the high retention of divalent anions over monovalent (Ballet et al., 2007).

The combined use of Spiegler–Kedem model and the SHP model shows a perfect compatibility and a good correlation with experimental retention values of the solutes: NaH_2PO_4 and Na_2HPO_4 , depending on the solvent flux. The reflection coefficient σ and solute permeability P_s could, thus, be determined for each of phosphate salts (Table 2).

5. Pressure effect

Nanofiltration tests were performed on solutions of Na_2HPO_4 , NaH_2PO_4 at different concentrations, that is: 20, 100, and 1000 ppm. Figs. 6 and 7 display the evolution of the retention rate of phosphate ions H_2PO_4^- and HPO_4^{2-} according to the pressure applied to the membrane at 25 °C. The retention rate increases with pressure at first, then stabilizes and eventually reduces. Some authors (Paugam, 2002; Tsuru et al., 1998; Xu and Spencer, 1999) also reported the passage by a maximum retention rate which was attributed to the effect of a sharp increase in the polarization layer with the pressure at low tangential flow velocity.

The counter-ions Na^+ are characterized by a small ionic radius (0.095 nm) and relatively low hydration energy (407 kJ mol⁻¹) Paugam, 2002. They can get inside the membrane pores of about 1 nm in size where they are partially captured by the membrane surface forces (including both friction forces and electrostatic forces). In fact, at working pH values, the membrane can be regarded as negatively charged. When the pressure increases, the surface forces remain constant whereas the training forces toward the permeate increase because of the increasing velocity in pores.

At low pressures, surface forces are more important than training forces. In this case, the counter-ion and phosphate co-ions fluxes remain low so as to keep electroneutrality. Nevertheless, the solvent flux continues to increase with pressure and leads to a decrease in the solute concentration in the permeate and thus increasing its retention rate. Beyond a certain pressure, the training forces of the solute become greater than the surface forces, hence, the solute transport increases and leads to a decrease in retention rates.

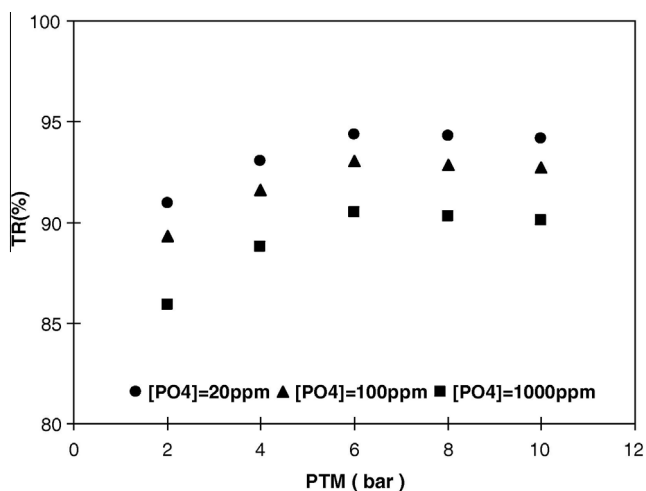


Figure 6 Pressure effect on the retention rate of the phosphate anions H_2PO_4^- at various concentrations.

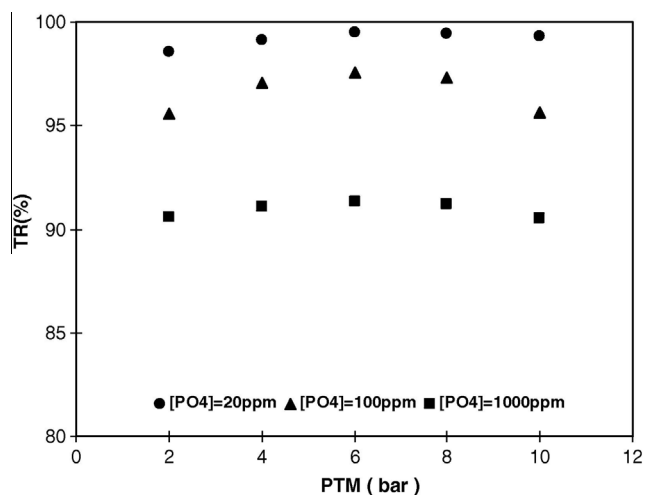


Figure 7 Pressure effect on the retention rate of the phosphates anions HPO_4^{2-} at various concentrations.

6. Effect of the ionic strength

The effect of the ionic strength on phosphate retention is characterized by a lower rejection rate of H_2PO_4^- anions [94% \rightarrow 88%] (Fig. 8) and HPO_4^{2-} anions [99% \rightarrow 91%] (Fig. 9) for an increase in ionic strength [0.20 \rightarrow 11] and [0.60 \rightarrow 32] mmol/L, respectively. Figs. 10 and 11 show the retention of the salts: Na_2HPO_4 and NaH_2PO_4 as a function of the permeate flux for different ionic strengths of the initial solution in the feed. The results reveal that the electrolyte retention rate decreases when ionic strength increases. This well-known behavior (Chaabane et al., 2006; Wang et al., 1997; Paugam et al., 2005) is a characteristic of charged membranes and is generally explained by the phenomenon of screening, that is, increasing the formation of an electrostatic shield, by counter-ions (Na^+), on the surface of the membrane. This neutralizes the negative charges of the membrane and reduces the retention of phosphate anions.

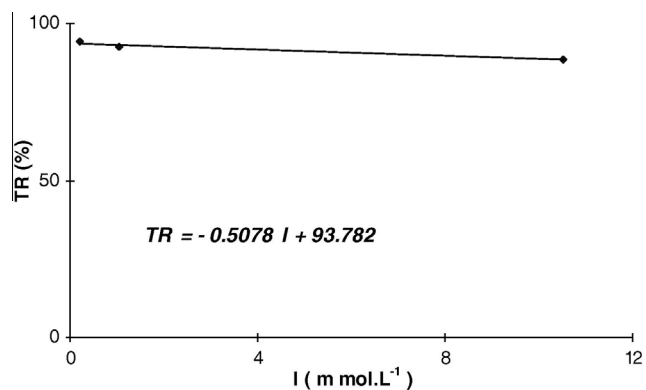


Figure 8 Ionic strength effect on the retention rate of the phosphates anions H_2PO_4^- .

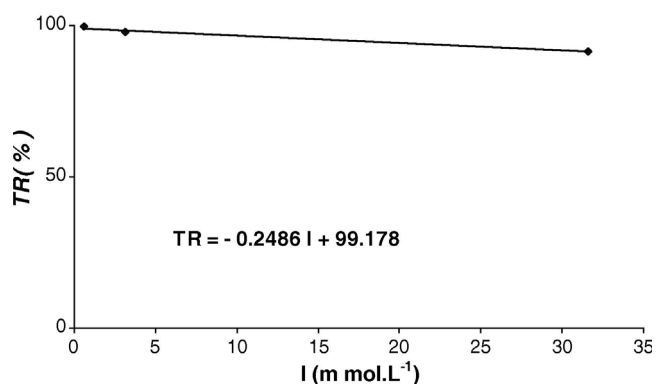


Figure 9 Ionic strength effect on the retention rate of the phosphates anions HPO_4^{2-} .

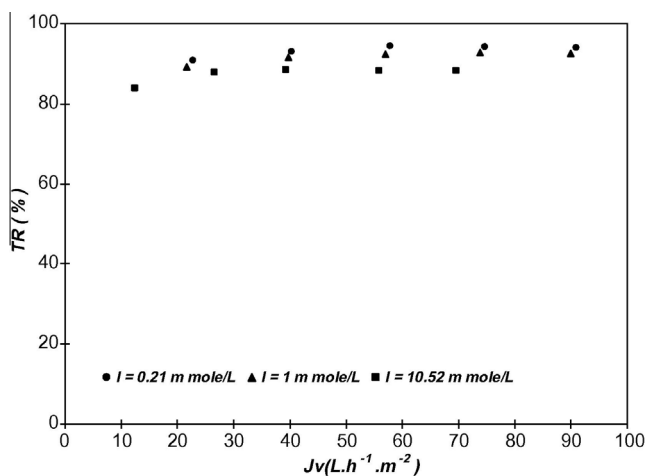


Figure 10 Ionic strength effect on the retention rate of the phosphates anions H_2PO_4^- as function flux.

In fact, the fixed charges of the active layer of the membrane are partially inhibited by the electrolyte counter-ions located in their vicinity. This screening is even stronger if these counter-ions are numerous. The repulsive forces between the membrane negative sites and the co-ions (H_2PO_4^- , HPO_4^{2-}) are, therefore, reduced. At low concentration, the shielding

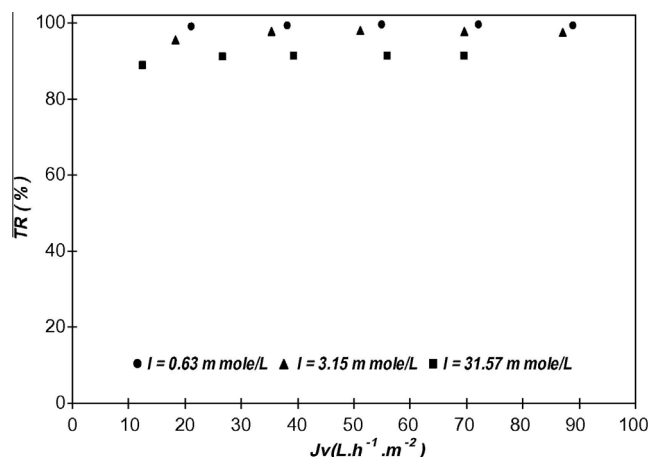


Figure 11 Ionic strength effect on the retention rate of the phosphates anions HPO_4^{2-} as function flux.

effect is very low. The repulsion of anions is important and leads to higher retention.

At higher concentration, the screen effect is amplified and the membrane potential decreases. As a result, the repulsion between the membrane and co-ions decreases. The co-ions cross the membrane more easily and carry the counter-ions to keep the electroneutrality, hence, the retention decreases.

7. Effect of pH

The effect of pH on the performance of the nanofiltration was investigated by many authors (Paugam et al., 2005; Qin et al., 2004; Seide et al., 2001; Nilsson et al., 2008). This parameter can affect the membrane properties (surface charge, hydrophobicity, and porosity) and chemical characteristics of the solutes.

Phosphate retention was studied for a concentration of 100 mg L^{-1} under 10 bars. The results (Fig. 12) show that the rejection rate increases from 40% to 82% when the solu-

tion pH varies from 2.9 to 5.9. This change reflects a fluctuating sign (positive/negative) of the membrane at the isoelectric point ($\text{pI} = 4.9$). On the other hand, the reading of the diagram (Fig. 13) shows that at pH less than 4, the phosphates are retained as H_3PO_4 ($R(\text{H}_3\text{PO}_4) = 40\%$). This induces a positive retention of H^+ , $R(\text{H}^+) = 46\%$ and a negative retention of monovalent phosphate anions $R(\text{H}_2\text{PO}_4^-) = -5\%$ to offset the charge imbalance created between the solution and the membrane. At pH values between 4.9 and 6, the phosphates rejection rate reached 82% in the form of anions H_2PO_4^- ($R = 98\%$) and H_3PO_4 ($R = 12\%$). The large increase observed in the rejection of phosphate is likely caused by a combination of the increase of phosphate anions percentage mainly H_2PO_4^- and the membrane charge becoming increasingly negative.

The evolution of pH value with respect to phosphoric acid pK_{a1} generates different forms of phosphates and the retention occurs in tune with this variant. In fact, at $\text{pH} = 6$ and $\text{pK}_{a2} = 7.2$, phosphates exist as H_2PO_4^- with a rejection rate of about 98%. The condition of electroneutrality of the system (membrane–solution) is verified by the retention value of Na^+ ($R = 98\%$). This observation is apparent for pH values more than pK_{a2} with equal coexistence of the two forms of phosphate H_2PO_4^- ($R = 99\%$) and HPO_4^{2-} ($R = 99\%$) in the retentate at $\text{pH} = 10.23$. Beyond this value it is the divalent form of phosphate anions HPO_4^{2-} which is prominent with a retention of about 99%. Similar results are obtained by Ballet et al. (2007) for the same pH range with the NF200 membranes.

8. Conclusion

This study enables a possible selective nanofiltration separation of monovalent and bivalents phosphate ions (H_2PO_4^- and HPO_4^{2-}) present in urban and industrial water.

The membrane selectivity vis-à-vis the ions leads to assert that the bivalent phosphate ions are better retained than monovalent, especially at low-pressure where chemical selectivity is predominant, even for solutions of high ionic strength.

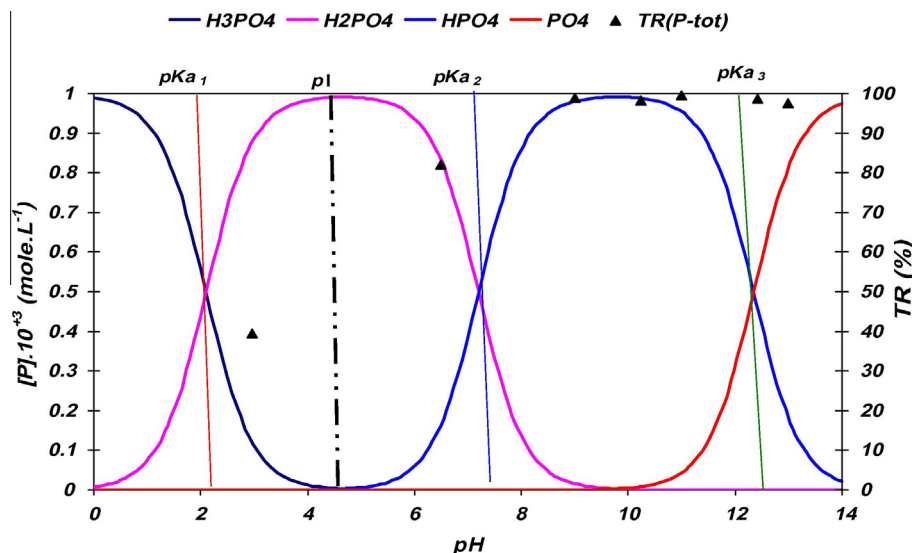


Figure 12 Effect of pH on the evolution of the phosphate retention rate on the diagram of species prevalence.

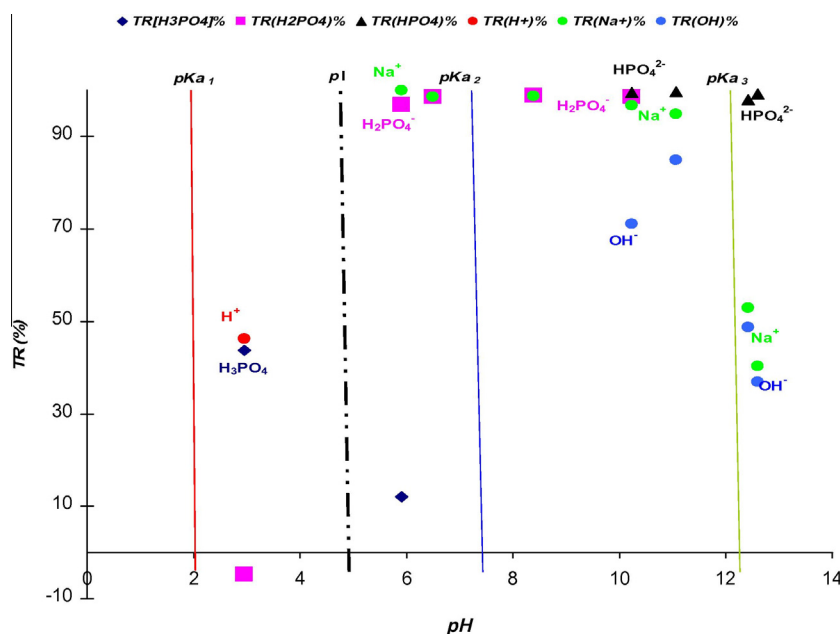


Figure 13 Retention rate of various phosphate species as function of pH.

The ion charge (sign and valence), compared with the sign of the membrane active groups, is a predominant element in the retention of ions. Actually, the divalent co-ion HPO_4^{2-} is strongly retained and the counter-ion Na^+ may partly screen the membrane residual ionized groups of the membrane until reversing its potential sign.

The monovalent co-ions H_2PO_4^- cross even better the membrane because of their high mobility and low number of membrane-ionized groups. The high retention of a divalent co-ion also induces a higher transmission in co-ions and monovalent counter-ion, so as to compensate the charge imbalance.

The phosphate transfer across the Nanomax-50 membrane is done via a dual mechanism, one physical by convection and the other chemical by diffusion. Selectivity or sharing between the different phosphate anions (H_2PO_4^- , HPO_4^{2-}) is controlled by an interplay between the steric effect and electrostatic exclusion.

By varying the operating parameters (TMP, ionic strength, pH), it is possible to favor one or the other of two mechanisms. The ion transfer mechanisms proposed in this study should enable a better understanding of the selectivity observed during nanofiltration. However, it appears necessary to validate these results with studies on solutions of increasing complexity, before we can actually implement on waste effluent.

Nanofiltration is then a technique particularly complex at the fundamental level. Nevertheless, it is easier to implement, technically, since it enables to work at lower pressures. The theoretical difficulty lies in the fact that it is a transition technique between reverse osmosis and ultrafiltration where the two transfer mechanisms coexist and interfere. A major effort to simplify the “modeling” of phenomena is therefore essential to understand the fundamental mechanisms of phosphate transfer. This difficulty, due to the dual mechanism, is the richness of this technique because it allows the modulation of selectivity by varying the operating parameters, i.e. by promoting one or other of these two mechanisms each with its own selectivity.

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